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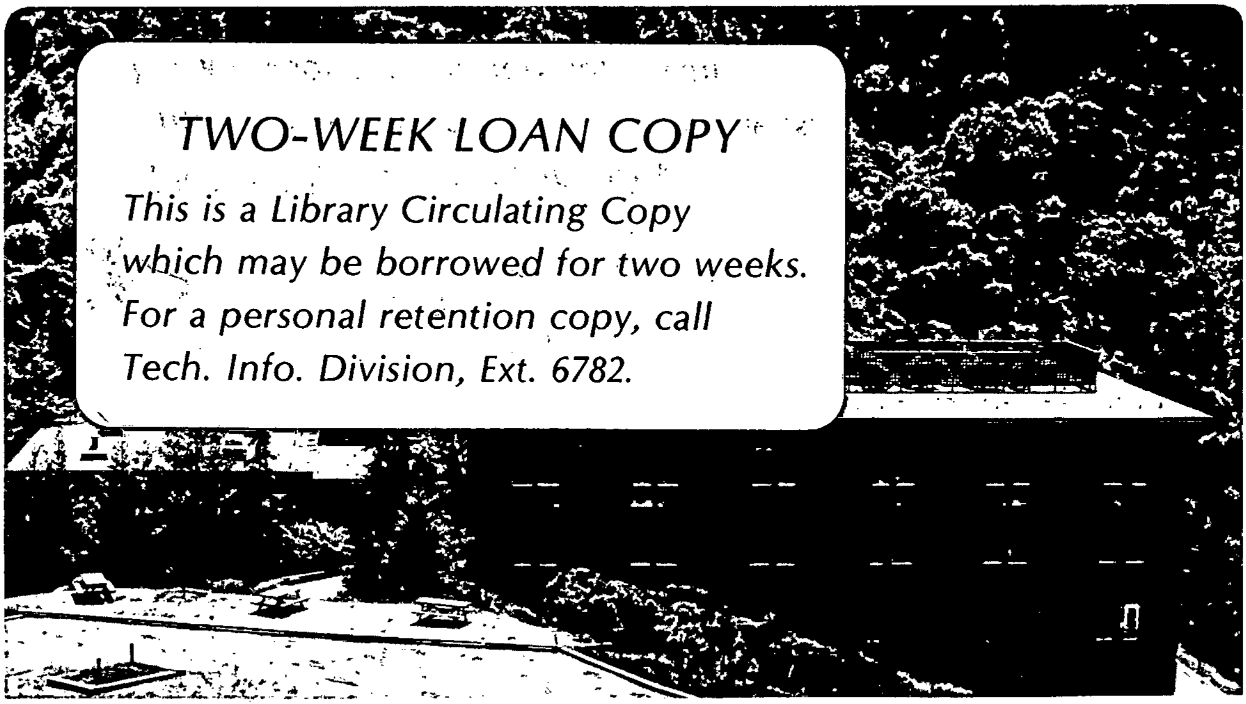

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1,1 Dilithioethylene: A Ground State Triplet Olefin with Nearly Free Rotation about the Double Bond

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Abstract

Molecular electronic structure theory has been applied to the $CLi_2=CH_2$ molecule 1,1 dilithioethylene. Both planar and triplet structures were considered for each of the lowest singlet and triplet electronic states. Geometry optimizations were carried out at the self-consistent-field (SCF) level of theory using a basis set of better than double zeta quality: C(9s 5p 1d/4s 2p 1d), Li(9s 4p/4s 2p), H(4s/2s). The predicted C=C bond distances are 1.356 Å (planar singlet), 1.334 Å (twisted singlet), 1.322 Å (planar triplet), and 1.323 Å (twisted triplet). The analogous Li-C-Li bond angles are 133.6°, 104.1°, 73.9°, and 75.5°, while the corresponding C-Li bond distances are 2.000 Å, 1.866 Å, 2.106 Å, and 2.064 Å. SCF theory predicts the twisted triplet to be the ground state, followed energetically by the planar triplet (1.2 kcal), twisted singlet (28.4 kcal), and planar singlet (29.3 kcal). The effects of electron correlation were investigated by configuration interaction (CI) including single and double excitations. The ordering of states is unchanged, with the relative energies being 0.0, 1.4, 14.0, and 15.5 kcal. After Davidson's correction for the effects of unlinked clusters, the same relative energies become 0.0, 1.4, 10.5, and 12.5 kcal. Qualitative features of the CLi_2CH_2 electronic structures are discussed in terms of orbital energies, Mulliken populations, and predicted dipole moments.

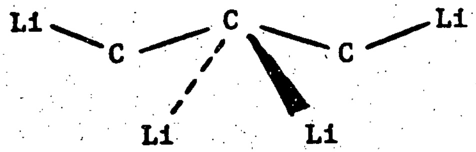
Introduction

In recent years Schleyer, Pople, and their colleagues have made some remarkable predictions concerning the equilibrium geometrical structures of lithiated hydrocarbons.[1-4] For example, the planar form of dilithiomethane CH_2Li_2 was predicted[2] to lie only a few kcal/mole above the conventional "tetrahedral" isomer. More complete theoretical studies of CH_2Li_2 have resoundingly confirmed this qualitative prediction and suggested[5] the following order for dilithiomethane electronic states:

planar triplet	5.9 kcal
tetrahedral triplet	4.7 kcal
planar singlet	4.2 kcal
tetrahedral singlet	0.0 kcal

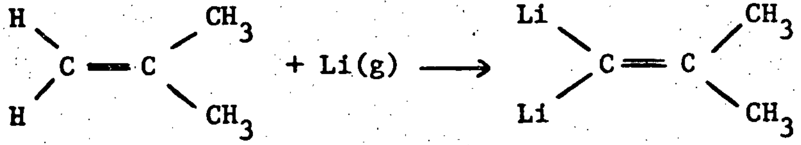
Although the above predictions are probably still only reliable to ± 3 kcal, it is clear that there is a near degeneracy of isomers and electronic states. Further, the barrier separating the planar and tetrahedral singlet states is small, of the order of 1 kcal (from the planar side).

In a second key paper Apeloig, Schleyer, Binkley, and Pople[3] (ASBP) have predicted equally unexpected properties for the olefin 1,1 dilithioethylene. These results are if anything more important since related molecules have already been prepared in the laboratory.[6-8] For example, the reaction of lithium atoms with $CC\ell_4$ at 800°C yields the product tetralithioethylene[6] C_2Li_4 to the extent of ∿ 60%. However, considering the remarkable structure predicted by Jemmis, Poppinger, Schleyer, and Pople[4b] for C_3Li_4



(1)

it is not clear that C_2Li_4 contains a "normal" C=C double bond. In related work it has been shown that the reaction of 2-methylpropene with n-butyllithium and potassium t-amyloxide[7] leads to dimetallation on the methyl group. It appears that the clearest experimental evidence for a lithiated olefin comes from the research of Morrison, Chung, and Lagow.[8] They found the reaction of isobutene with gaseous lithium atoms to give a ∿ 20% yield of the 1,1 dilithio compound



(2)

In their paper ASBP note that not only is the rotational barrier about the C=C double bond low, but the triplet or perpendicular form may even be the true equilibrium geometry. The primary conclusions of ASBP are summarized in Table I. Although ASBP note[3] that the theoretical methods chosen artificially favor triplet states relative to singlets, the predicted triplet-singlet energy separations were thought to be so large as to suggest a triplet ground state for CH_2CLi_2. This is also experimentally significant since it would allow identification of CH_2CLi_2 by matrix isolation electron spin resonance techniques.[9]

We consider the ASBP predictions[3] for 1,1 dilithioethylene to be sufficiently unorthodox and the possibility of laboratory preparation of this species sufficiently high to mandate further theoretical studies of this intriguing molecule. In the present work the theory has been pushed to essentially state-of-the-art levels of reliability through (a) extensions of the basis set and (b) an explicit description of the effects of electron correlation. In addition some qualitative aspects of the electronic structure of $CH_2=CLi_2$ are discussed in terms of dipole moments, Mulliken populations, and orbital energies.

Theoretical Approach

Throughout the present research a basis set of nearly double zeta plus polarization quality was employed. This means that in addition to two sets (p_x,p_y,p_z) of p functions on each lithium atom, a set of d functions was included on each carbon atom. The basis set thus chosen may be labeled C(9s 5p 1d/4s 2p 1d), Li(9s 4p/4s 2p), H(4s/2s). The carbon sp and hydrogen s sets are Dunning's contractions[10] of Huzinaga's primitive gaussian basis sets.[11] The carbon d function orbital exponent was $\alpha = 0.75$. The scale factor on the hydrogen s functions was 1.0, i.e., the gaussian exponents were just those of Huzinaga. Finally the lithium basis set is that given by Dunning and Hay.[12] Before concluding, it should be conceded that this basis set would have been better balanced had a set of p functions on each H atom been appended. However, the methylene (CH_2) group is the least interesting part of $CH_2=CLi_2$ from a structural and energetic viewpoint, and the truncation of the basis set to its present form was considered justifiable.

All geometry optimizations were carried out at the self-consistent-field (SCF) level of theory. This was done separately for the planar singlet, planar triplet, twisted singlet, and twisted triplet structures. Thereafter, single calculations were carried out on each of these four points allowing for consideration of electron correlation effects. This procedure is analogous to that adopted by ASBP,[3] who completed structural optimizations at the minimum basis SCF level and followed these with single calculations at the double zeta SCF level of theory.

The orbital occupancies for the four electronic species are:

planar singlet

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^2\ 4a_1^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 1b_1^2\ 3b_2^2 \tag{3}$$

tetrahedral singlet

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^2\ 4a_1^2\ 5a_1^2\ 1b_1^2\ 6a_1^2\ 2b_2^2\ 2b_1^2 \tag{4}$$

planar triplet

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^2\ 4a_1^2\ 5a_1^2\ 2b_2^2\ 6a_1^2\ 1b_1^2\ 3b_2\ 7a_1 \tag{5}$$

and twisted triplet

$$1a_1^2\ 2a_1^2\ 3a_1^2\ 1b_2^2\ 4a_1^2\ 5a_1^2\ 1b_1^2\ 6a_1^2\ 2b_2^2\ 2b_1\ 7a_1 \tag{6}$$

The effects of electron correlation were taken into account via configuration interaction (CI) including all single and double excitations. For the triplet states, only those doubly-excited configurations having nonzero Hamiltonian matrix elements[13] with (5) or (6) were included. In addition the CI was restricted by holding the four lowest orbitals (corresponding to C and Li 1s atomic orbitals) doubly-occupied in all configurations. Finally the two highest virtual orbitals were deleted entirely from the CI procedure. In this manner the total numbers of configurations treated variationally were 8984 (planar singlet), 8509 (tetrahedral singlet), 11,799 (planar triplet), and 11,169 (twisted triplet).

The CI wavefunctions were obtained using the direct CI methods of Lucchese,[14] as incorporated in the BERKELEY system of programs.[15] For the largest computation, the planar triplet, the SCF procedure all-inclusive required 160 minutes, the integral transformation 135 minutes, and the CI 331 minutes.

For the final estimates of the electronic energy separations, Davidson's correction[16] for unlinked clusters was adopted. Therein the contribution ΔE_Q of quadruple excitations to the correlation energy is given by

$$\Delta E_Q = (1-C_0^2)\Delta E_{SD} \tag{7}$$

where C_0 is the coefficient of the self-consistent-field (SCF) wavefunction in the CI expansion and ΔE_{SD} is the correlation energy due to single and double excitations. This formula has proven to be quite reliable in predictions of the singlet-triplet separation of methylene.[17,18]

Structural Results

All bond distances were predicted to within a precision of 0.001 Å and bond angles were optimized to within 0.1°. For the four electronic states examined here, the theoretical structures are illustrated in Figures 1 and 2. To discuss these structures, we show for comparison in Figure 3 the analogous geometries[5] for planar and "tetrahedral" (or twisted) dilithiomethane.

The most conventional feature of the triplet geometries (Figure 1) is their 1.094 Å CH bond distance. The HCH bond angles of 115.2° (twisted) and 114.8° (planar) are also fairly "normal", as compared to 116.6° observed experimentally[19] for ethylene. For reasons which will become apparent later, the fact that both triplet C-C bond distances (1.323 and 1.322 Å) are actually somewhat <u>shorter</u> than the ethylene value[19] of 1.330 Å is quite remarkable. This would seem to imply that, if anything, the C-C bond is a bit <u>stronger</u> than conventional carbon-carbon double bonds.

The most interesting feature of the triplet structures is that both have very acute LiCLi bond angles, namely 75.5° and 73.9°. Although these angles are unprecedented in hydrocarbon chemistry, the very same qualitative result was found[2,5] for triplet CH_2Li_2. These angles are sufficiently acute that they suggest that the CLi_2 fragment could possibly be considered a three-membered ring. In this light, the Li-Li bond distances for the twisted and planar structures are 2.527 and 2.532 Å. And in fact these distance are <u>less</u> than the conventional Li-Li bond distance of 2.67 Å known experimentally[20] for Li_2. It would not be unreasonable, therefore, to conclude that there is a single bond between the two Li atoms in triplet 1,1 dilithioethylene.

The last noteworthy structural feature of the triplet conformations is the C-Li distance, 2.064 Å and 2.106 Å for the twisted and planar cases, respectively. These distances should perhaps first be compared to the 2.02 Å in methyllithium,[21] a more conventional lithiocarbon. We thus conclude that these triplet C-Li distances are on the long side. However, for triplet dilithiomethane, long C-Li distances were also found. In that case, however, the twisted conformation had the longer C-Li bond distance. Nevertheless, all this fits into a nice pattern if it is realized that (a) the two "expected" triplet conformations (planar CLi_2CH_2 and twisted CLi_2H_2) have the longer C-Li distances 2.106 Å and 2.128 Å, while (b) the "unexpected" triplet conformations (twisted CLi_2CH_2 and planar CLi_2H_2) have the shorter C-Li distances 2.064 Å and 2.069 Å.

Turning now to the singlet structures, it is seen first in Figure 2 that the C-H distances of 1.101 Å (twisted) and 1.108 Å (planar) are notably longer than those for the corresponding triplet geometries. In fact these C-H distances approach the length of any known experimentally. For example the very long CH distance[22] in the CH^+ diatomic ion is 1.131 Å.

The singlet C=C distances, 1.334 Å (twisted) and 1.356 Å (planar), while 0.011 Å and 0.032 Å longer than the analogous triplet distances, still fall in the middle of the range for carbon-carbon double bonds. In this regard, it is worth noting that while these predicted bond distances are only reliable to within ∿ 0.01 Å, the theoretical bond distance <u>differences</u> should be more accurate.

For the singlet electronic states, the predicted LiCLi bond angles are much larger than the ∿ 75° angles found for the triplets. However, the unexpected result is the difference of 29.5° between the twisted (104.1°) and planar (133.6°) conformations. For the same parameters ASBP[3] predicted 108.8° and 119.8° bond angles. This difference in LiCLi bond angles is also seen for dilithiomethane[5] where the twisted singlet angle (120.3°) is 18.6° larger than the planar singlet result (101.7°). Again we see that the planar substituted ethylene is properly related to the twisted (or "tetrahedral") substituted methane.

The singlet C-Li distances 1.866 Å (twisted) and 2.000 Å (planar) are respectively 0.198 Å and 0.106 Å shorter than the corresponding triplet distances. This suggests that the C-Li bonds are stronger for the singlet states than for the triplets. However, as we shall see, this apparent inequity is more than compensated by the triplet Li-Li bonds, which have no direct counterpart in the singlet conformations. That is, the shorter of the two Li-Li singlet distances is 2.943 Å (twisted singlet), notably longer than the 2.673 Å observed for Li_2. For the planar singlet, the Li-Li distance is even longer, 3.677 Å.

Energetic Results

The present energetic results are summarized in Table II. At the SCF level of theory, the twisted triplet is predicted to be the absolute minimum of the CLi_2CH_2 potential energy surface. However, the planar triplet lies only 1.2 kcal higher. The tetrahedral singlet and planar singlet lie much higher, at 28.4 and 29.3 kcal, respectively. It is clear that for both electronic states, the planar and twisted conformations are nearly degenerate.

Our SCF relative energies are generally in good agreement with those of ASBP.[3] In fact their twisted triplet-planar triplet separation of 1.1 kcal is nearly identical to the present 1.2 kcal, although the latter result was obtained with a notably larger basis set. The only qualitative differences between our work and the ASBP predictions are (a) their 4-31G singlet relative energies are a bit higher (5.9 kcal and 4.2 kcal) and (b) they predict the planar singlet to be slightly (0.8 kcal) lower than the twisted conformer.

As expected,[3] the primary effect of electron correlation is to lower the singlet states relative to the corresponding triplets. Table II shows that the order of the four electronic moieties is not changed with respect to the SCF predictions. Furthermore, the tetrahedral triplet-planar triplet energy difference is virtually unaffected by electron correlation, the three predictions being 1.2 kcal (SCF), 1.4 kcal (CI), and 1.4 kcal (unlinked cluster corrected). Thus we are able to unequivocally predict a twisted triplet ground state for 1,1 dilithioethylene.

At the CI level of theory the two singlet states are lowered by ∿ 14 kcal/mole relative to the analogous triplets. Use of the Davidson correction[16] for quadrupole excitations results in further lowerings of 3.0 kcal (planar singlet) and 3.5 kcal (twisted singlet) relative to the twisted triplet ground state. Thus we arrive at our final prediction that the two singlet conformers, i.e., at 10.5 and 12 kcal above the triplet ground state. Comparison with the ASBP predictions of Table I indicates that relative to previous theoretical work,[3] the twisted triplet-twisted singlet separation has been reduced from 34.3 kcal to 10.5 kcal. Comparisons of this type are particularly valuable, since they provide guidelines for the adjustment of future theoretical predictions on systems too large to make possible the use of levels of theory as sophisticated as the present.

Electronic Structure Considerations

One of the more obvious ways of examining the electronic structure of a molecule is via the orbital energies, related via Koopman's Theorem to the ionization potentials. These are seen in Table III. For the closed-shell singlets, it is readily apparent that the $3b_2$ (planar) and $2b_1$ (twisted) are the highest occupied molecular orbitals (HOMO's) for the two conformations. It is relatively easy (ionization potentials 4.8 and 4.5 eV, respectively) to "remove" an electron from either of these orbitals. However when one of the HOMO electrons is replaced by the closed-shell LUMO to yield the lowest triplet, the single $3b_2$ or $2b_1$ electron becomes significantly more difficult to remove.

If one were naive enough to take Koopmans' Theorem literally and the singlet and triplet structures were identical, the singlet-triplet separations may be predicted as

$$\Delta E(\text{planar}) = \varepsilon_{3b_2}(^1A_1) - \varepsilon_{7a_1}(^3B_2) \qquad (8)$$

$$\Delta E(\text{twisted}) = \varepsilon_{2b_1}(^1A_1) - \varepsilon_{7a_1}(^3B_1) \qquad (9)$$

since the final ionic states are identical in electron configuration. However, the striking geometry differences noted above preclude this possibility. Nonetheless, this simple procedure does correctly predict the triplet state to lie below the singlet for both planar and tetrahedral conformations.

Mulliken population analyses are summarized in Table IV. Although this simple breakdown is of little <u>absolute</u> value, trends relating different electronic states and different isomers should be meaningful with the basis sets adopted in this research.

One of the more obvious trends is the fact that the CLi_2 carbon has more electron density associated with it than does the methylene carbon. This is clearly related to the fact that the former C atom gains Mulliken electrons at the expense of the adjacent electropositive Li atoms. In any case, for the singlet conformers, there is a high degree of local polarity in the vicinity of the CLi_2 group.

The latter fact is reflected in the large dipole moments predicted for the planar singlet (5.27 debye) and tetrahedral singlet (5.20 debye). However the triplet dipole moments are radically smaller, 0.59 and 1.35 debye, respectively, and of the opposite sign, as seen in the last column of Table IV. This abrupt change in dipole moments is seen to a lesser degree in the Mulliken populations. For example, we see for the tetrahedral structures

$$\begin{array}{c} -0.98 \quad +0.92 \\ \mathrm{C} - \mathrm{Li_2} \\ \text{singlet} \end{array} \longrightarrow \begin{array}{c} -0.66 \quad +0.66 \\ \mathrm{C} - \mathrm{Li_2} \\ \text{triplet} \end{array} \qquad (10)$$

In the former (singlet) case, the large CLi_2 local polarity far outweighs the CH_2 dipole of the opposite direction, but for the triplets the converse is true. The dipole moments have also been investigated at the CI level, where correlation effects are shown to decrease the singlet dipole moments by ∿ 0.7 debye. The triplet dipole moments also shift in the $\overset{+}{\mathrm{H_2C}}\,\overset{-}{\mathrm{C}}\mathrm{Li_2}$ direction when electron correlation is described. However, in this case the differential effect is only ∿ 0.2 debye, making the predicted ground state (twisted triplet) dipole moment -1.58 debye.

The lower portion of Table IV sets out in some detail the characteristics of the unpaired orbital of the two triplet conformers. These data are critical first of all because $CLi_2=CH_2$ is likely to be first observed by matrix isolation electron paramagnetic resonance (EPR) spectroscopy.[9] This technique is often capable of yielding qualitative information concerning the nature of the unpaired orbitals. In addition, this detailed Mulliken analysis allows an explanation of the much smaller triplet state dipole moments.

In going from the singlet to the triplet electronic states, the electron configuration change

$$b^2 \rightarrow ba \tag{11}$$

occurs. Thus the highest occupied b orbital loses one electron and the lowest unoccupied a orbital becomes singly-occupied. Table IV shows that this $7a_1$ orbital (for both planar and twisted geometries) is almost exclusively lithium-like in character. In striking contrast, the b orbital in (11) is predominantly carbon 2p-like. Thus the single excitation b → a radically reduces the C^-Li^+ polarity of the CLi_2 fragment and correspondingly reduces the total dipole moment of 1,1 dilithioethylene. This simple argument also explains the remarkably short Li-Li distance (essentially a single bond) observed for the triplet states. The $7a_1$ orbital is an Li-Li bonding orbital.

Concluding Remarks

1,1 dilithioethylene has been shown to have a twisted triplet ground state (Figure 1), with the planar triplet conformation lying only ∿ 1.4 kcal higher. An obvious final question concerns the size of the barrier to rotation about what is formally a C═C double bond. This rotational coordinate θ has been examined for angles between 0° (planar) and 90° (twisted) and the results are summarized in Figure 3. There it is seen that there is no additional (i.e., in excess of the twisted-planar energy difference) triplet barrier to rotation. The resulting barrier of 1.4 kcal is certainly in striking contrast to the 60 kcal rotation barrier[23] for the unsubstituted ethylene.

The low rotational barrier and short Li-Li distance in the triplet state suggest that CH_2CLi_2 might be a σ complex of Li_2 and vinylidene. This contention is supported by the fact that the $^3B_2$ vinylidene C = C bond distance predicted[24] from the double zeta SCF level of theory is 1.324 Å, essentially indistinguishable from the 1.323 Å seen in Figure 1. The agreement for the CH distances and HCH angles is reasonable (0.018 Å and 2.4°, respectively) but not as striking.

After this work was submitted for publication, we learned that similar SCF studies (with similar results) of the singlet conformations of CH_2CLi_2 had been carried out by Kos and Schleyer.[25] These workers did not however consider the triplet conformations nor go beyond the Hartree-Fock level of theory.

We hope that these theoretical predictions, following those of Pople and Schleyer,[3] will motivate experimentalists to synthesize the gas-phase 1,1 dilithioethylene molecule. It seems apparent that matrix-isolation ESR techniques[9] are well suited to this task, and we look forward to experimental studies of this very unconventional molecule.

Acknowledgments

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Table I. Summary of the predictions of Apeloig, Scheleyer, Binkley, and Pople (ASBP)[3] for 1,1 dilithioethylene. Relative energies are given in kcal/mole. ASBP predicted all equilibrium geometries at the minimum basis set (STO-3G) self-consistent-field level of theory.

Species \ Basis Set	STO-3G	4-31G
Planar Singlet	36.7	33.5
Planar Triplet	2.1	1.1
Twisted[a] Singlet	26.8	34.3
Twisted[a] Triplet	0.0	0.0

[a] Elsewhere referred to as perpendicular or "tetrahedral".

Table II. Summary of energetic results for 1,1 dilithioethylene.

	Absolute Energies (hartrees)			Relative Energies (kcal/mole)		
	SCF	CI	Davidson Correction	SCF	CI	Davidson Correction
planar singlet	-91.67373	-91.93617	-91.96462	29.3	15.5	12.5
tetrahedral singlet	-91.67513	-91.93866	-91.96777	28.4	14.0	10.5
planar triplet	-91.71851	-91.95873	-91.98228	1.2	1.4	1.4
tetrahedral triplet	-91.72037	-91.96090	-91.98455	0.0	0.0	0.0

Table III. Orbital energies in hartrees (= 27.21 eV) for four electronic conformations of $CLi_2=CH_2$.

	planar singlet	planar triplet		tetrahedral singlet	tetrahedral triplet
$1a_1$	-11.1475	-11.2129	$1a_1$	-11.1841	-11.2286
$2a_1$	-11.0924	-11.1952	$2a_1$	-11.1282	-11.1957
$3a_1$	- 2.4071	- 2.4584	$3a_1$	- 2.4293	- 2.4562
$1b_2$	- 2.4071	- 2.4577	$1b_2$	- 2.4289	- 2.4554
$4a_1$	- 0.8840	- 0.9817	$4a_1$	- 0.9282	- 0.9908
$5a_1$	- 0.6116	- 0.6872	$5a_1$	- 0.6466	- 0.6966
$2b_2$	- 0.4834	- 0.5649	$1b_1$	- 0.5168	- 0.5746
$6a_1$	- 0.3428	- 0.4573	$6a_1$	- 0.3984	- 0.4624
$1b_1$	- 0.2553	- 0.3484	$2b_2$	- 0.3137	- 0.3648
$3b_2$	- 0.1754	- 0.3225	$2b_1$	- 0.1637	- 0.3062
$7a_1$	--	- 0.1867	$7a_1$	--	- 0.1819

Table IV. Mulliken populations and predicted dipole moments for 1,1 dilithioethylene.

	CH_2 Group					CLi_2 Group							
	C(s)	C(p)	C(d)	C(total)	H(s)	C(s)	C(p)	C(d)	C(total)	Li(s)	Li(p)	Li(total)	μ(Debye)
Total atomic populations													
planar singlet	3.23	2.94	0.05	6.22	0.92	3.61	3.24	0.03	6.88	2.32	0.21	2.53	5.27
planar triplet	3.29	3.06	0.05	6.39	0.84	3.55	3.01	0.03	6.59	2.39	0.28	2.67	- 0.59[a]
tetrahedral singlet	3.26	2.90	0.05	6.21	0.86	3.57	3.39	0.02	6.98	2.11	0.43	2.54	5.20
tetrahedral triplet	3.29	3.00	0.05	6.34	0.83	3.57	3.06	0.03	6.66	2.39	0.29	2.67	- 1.35[a]
Unpaired spin orbitals													
planar triplet													
$3b_2$	0.00	-0.03	0.01	-0.02	0.02	0.00	0.89	0.00	0.89	0.02	0.02	0.04	
$7a_1$	0.00	0.00	0.00	0.00	0.00	0.01	-0.03	0.00	-0.02	0.32	0.19	0.51	
tetrahedral triplet													
$2b_1$	0.00	-0.03	0.01	-0.01	0.02	0.00	0.91	0.00	0.91	0.00	0.03	0.03	
$7a_1$	0.00	0.00	0.00	0.00	0.00	0.00	-0.03	0.00	-0.03	0.33	0.18	0.51	

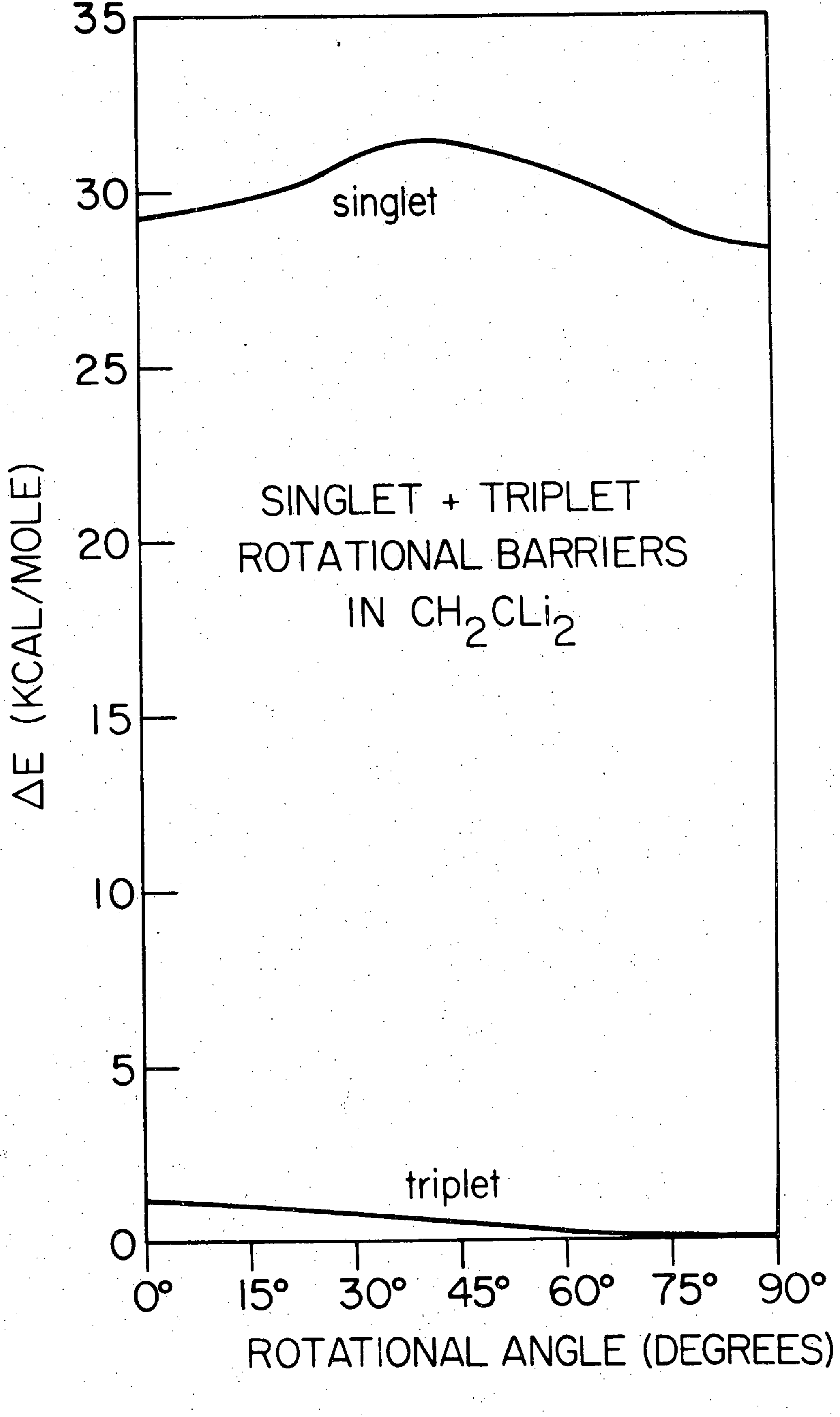
[a] Negative dipole moment implies $H_2\overset{+}{C}\overset{-}{C}Li_2$ polarity.

Figure Captions

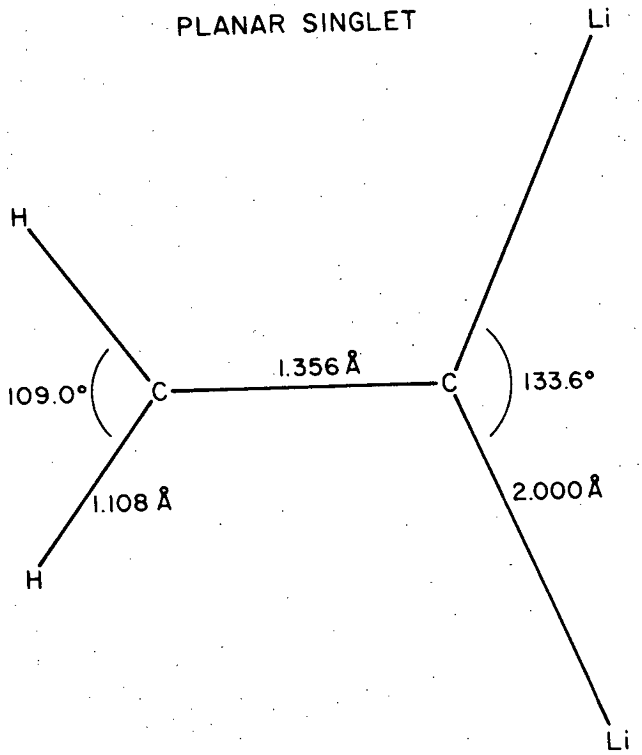
1. Predicted planar and twisted geometries for triplet 1,1 dilithioethylene. Bond distances are in angstroms.

2. Theoretical structures for the lowest singlet electronic state of CLi_2CH_2. Bond distances are in Å.

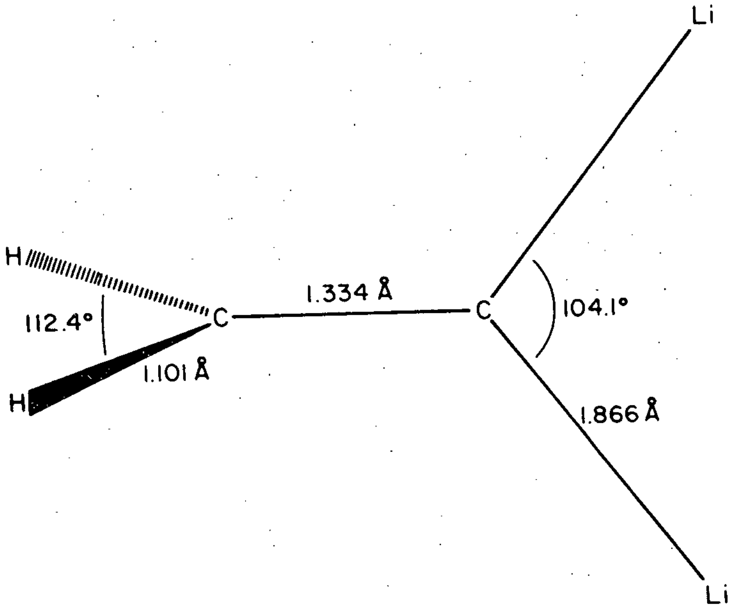
3. Potential curves for rotation about the C=C double bond of 1,1 dilithioethylene. The results were obtained at the single-configuration SCF level of theory.


35
30
25
20
15
10
5
0
ΔE (KCAL/MOLE)
singlet
SINGLET + TRIPLET
ROTATIONAL BARRIERS
IN CH2CLi2
triplet
0°
15°
30°
45°
60°
75°
90°
ROTATIONAL ANGLE (DEGREES)

PLANAR SINGLET



TWISTED SINGLET



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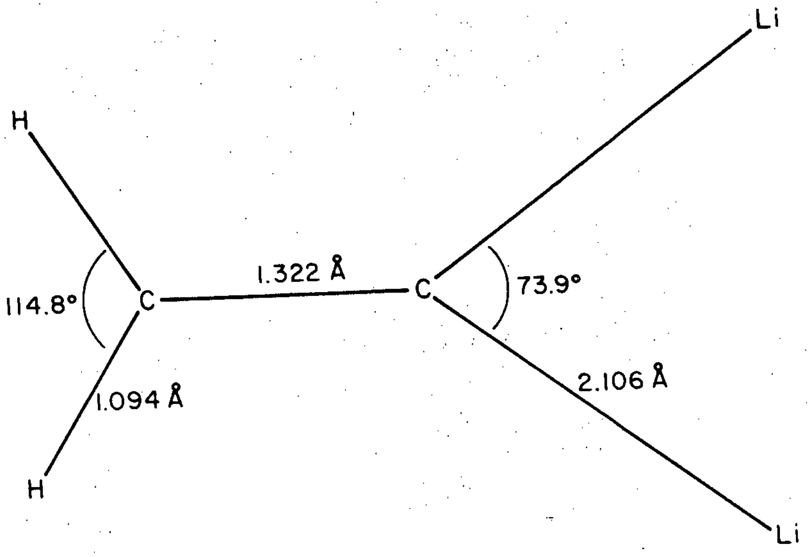
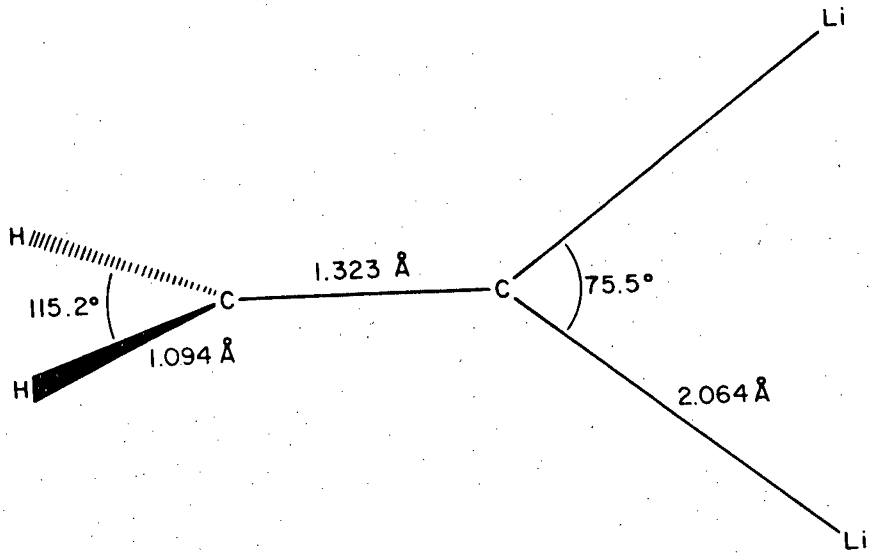
PLANAR TRIPLET



TWISTED TRIPLET



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